

Supporting Industry



Technical Highlights of the Analytical Chemistry Division of NIST

Chemical Measurement Technologies:

- Developed and critically evaluated new technologies for real-time chemical analysis of automobile exhaust
- Provided elemental concentration and profile information of light elements in thin films for high technology devices in industrial applications
- Developed method for doping metal samples with a known amount of hydrogen – one of the chief contributors to brittleness in metals – to be used to prepare an SRM needed in the monitoring and control of manufacturing processes
- Investigated bias in Karl Fischer methods of measuring moisture in transformer oils – a critical indicator in scheduling transformer maintenance for the electric power industry
- Developing NTRM program to support increasing standards needs of the metals industry
- Initiated microanalytical device program focused on identifying and overcoming barriers to their use for quantitative measurements

Standards Development and Quality Assurance Activities:

- Issued several new food SRMs to assist industry in complying with nutrition labeling laws
- Used approach developed to determine sulfur in the FY96 recertification of SRM 131f Low Alloy Steel (at nominal 4 $\mu\text{g/g}$ level) (with resulting 20-fold improvement in uncertainty) to screen nine aerospace industry-supplied superalloys and identified a suitable candidate SRM with sulfur concentration $<1\mu\text{g/g}$ needed as QA tool in the production and material qualification of superalloys for next generation jet engines
- Developed prototype rare-earth glass wavelength standard for process control instrumentation using the near-infrared spectral region
- Developed three new SRMs to support low-emission vehicle exhaust measurement
- Developed prototype reference material thin films of various thicknesses of titanium nitride on silicon substrates to calibrate X-Ray fluorescence measurements routinely used in the fabrication of semiconductors to monitor thin film deposition processes
- Certified ion-implanted As in silicon SRM for semiconductor industry
- Continued to provide cold neutron PGAA measurements of hydrogen for companies in the aluminum, petrochemical, computer and other high technology industries

Aerospace

Determination of Low-Level Sulfur In Aerospace Superalloys

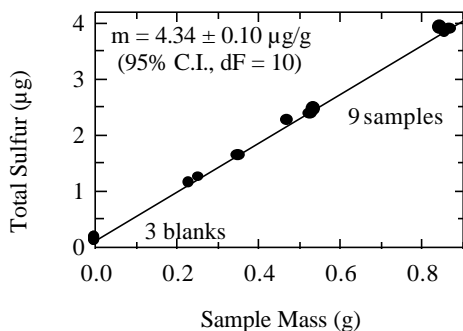


fig. 1

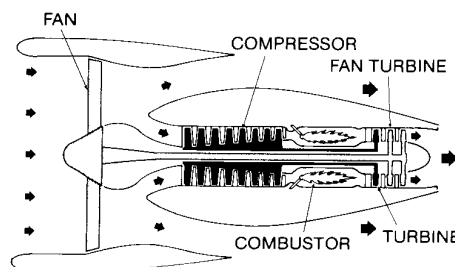


fig. 2

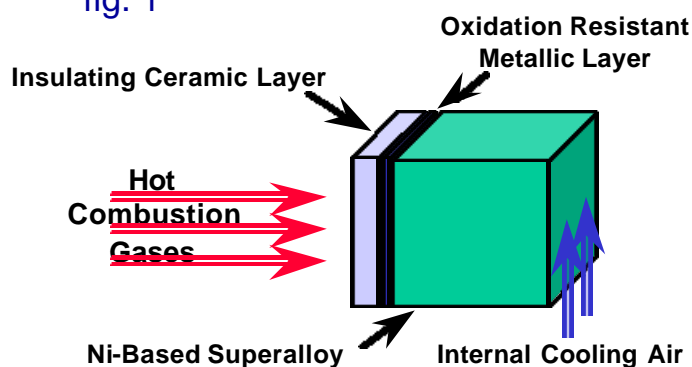


fig. 3

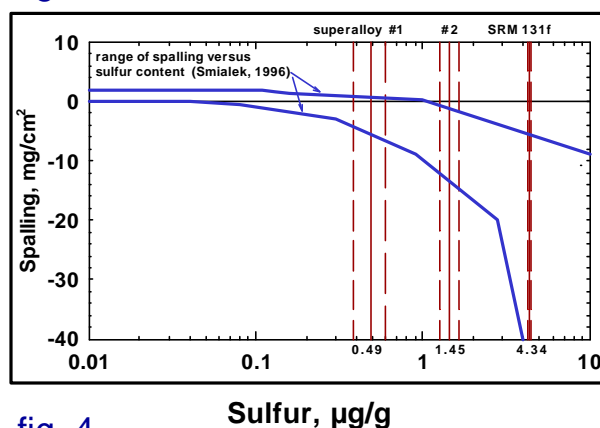


fig. 4

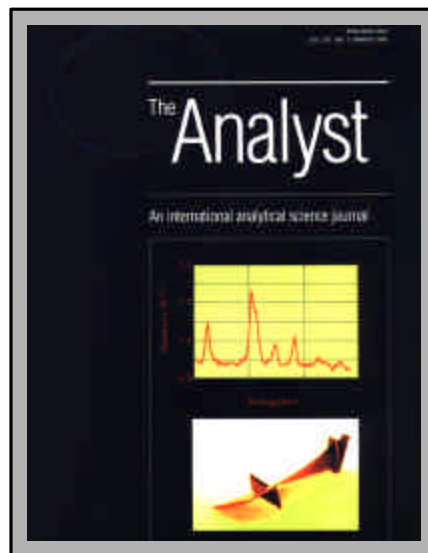
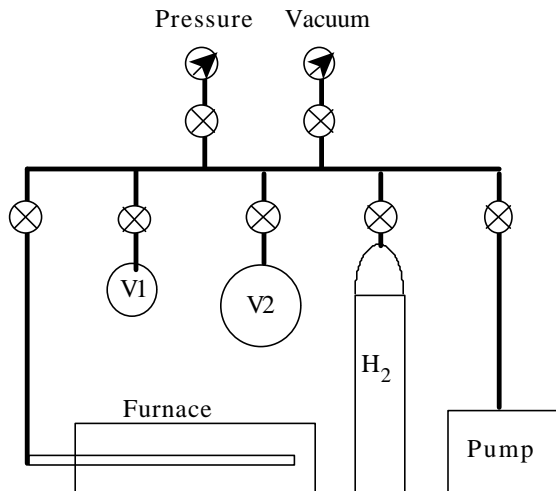
Project Description: To support the aerospace industry's need to measure accurately the sulfur content in Ni-based superalloys at 1 μg/g and below.

Results: SRM 131f ($4 \mu\text{g/g} \pm 2 \mu\text{g/g}$) is currently the *de facto* sulfur standard for the aerospace industry. It was recertified by ID-TIMS using a least squares regression technique at $4.34 \mu\text{g/g}$ with a 95% confidence limit of $0.10 \mu\text{g/g}$ which is a 20-fold improvement in uncertainty (fig. 1). It is believed that the uncertainty of $0.10 \mu\text{g/g}$ can be achieved at concentrations well below $1 \mu\text{g/g}$ sulfur. This approach was used to screen nine industry-supplied superalloys to identify a suitable candidate SRM with sulfur content $<1 \mu\text{g/g}$ needed by this industry.

Relevance: The inlet temperature of a high temperature turbine (fig. 2), the most critical component in a jet turbine, determines the power and efficiency of the engine. The adherence of the protective oxide coating (fig. 3,4) is enhanced by reducing the sulfur concentration below $0.5 \mu\text{g/g}$ in the superalloy. This will make possible the next generation of turbines which will have thermal barrier coatings permitting the operating temperature to be increased $\sim 200^\circ\text{C}$ resulting in fuel savings and increased longevity.

Aerospace

Standards for Hydrogen in Titanium Alloy



Project Description: To prepare and characterize prototype SRMs for hydrogen in titanium.

Result and Relevance: A procedure has been demonstrated for doping titanium alloy specimens with a known amount of hydrogen. In the reversible reaction $\text{Ti} + \text{H}_2 = \text{TiH}_2$, the equilibrium pressure is less than 10^{-11} kPa at room temperature and 1.5×10^4 kPa at 900 °C. Reaction is rapid at 300 °C. This gettering reaction with hot titanium is in common use in geochemistry for separating hydrogen from oxygen, nitrogen (which react irreversibly) and from noble gases. Massive hydrides are prepared industrially by the same direct reaction process for hydrogen-based energy storage and nuclear applications.

In the apparatus shown in the figure, means are provided for pumping away air and hydrogen from samples at high temperature and for admitting a known pressure of hydrogen in a calibrated volume at room temperature, then raising the temperature of the closed system to carry out the reaction. The amount of H in titanium alloy specimens doped with hydrogen was measured by cold-neutron prompt-gamma activation analysis and the results agreed with the quantity added -- demonstrating our capability for doping metal samples with hydrogen at predetermined target levels. The accuracy of the doping is limited by that of the pressure, better than 0.5%.

Impact: Hydrogen is one of the chief contributors to brittleness in metals; its control in manufacturing processes is crucial. SRMs are needed to calibrate and validate measurement methods in industrial use.

Semiconductor

Characterization of Thin Films for High Technology Applications Using Cold Neutron Depth Profiling

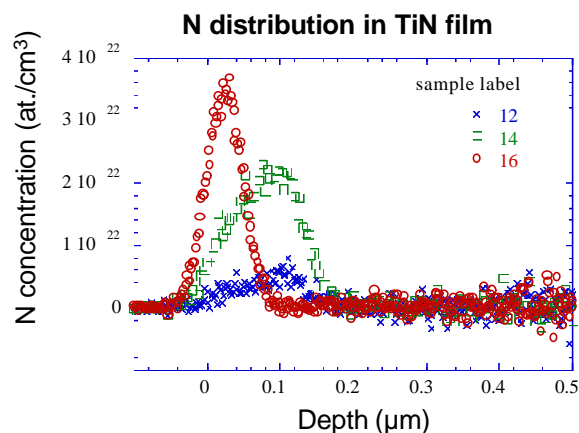


Fig. 1

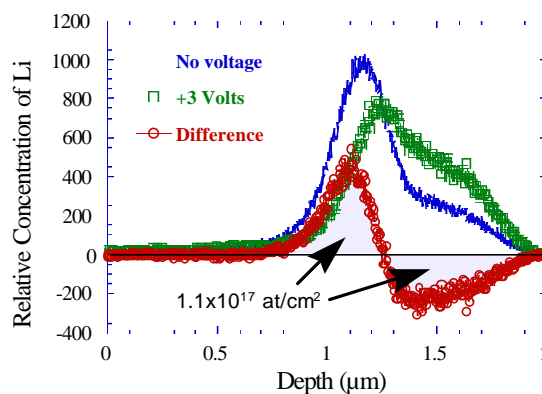


Fig. 2

Project Description: To provide elemental concentration and profile information of light elements in thin films for industrial applications. Two recent examples are shown.

Result and Relevance: Company A needed nitrogen profiles of thin TiN films used as adhesion layers in the semiconductor process. A series of films manufactured under different conditions was sent for analysis. Figure 1 shows the nitrogen profiles obtained for three of the thinnest of the Company A titanium nitride films. Clear differences in the profiles are observed.

Company B required measurements of the lithium concentration in an electrooptic multilayer. We were able to measure not only the concentration and depth of the lithium, but also observe the movement of the lithium as the potential across the film was changed. Figure 2 shows the lithium profile of a Company B multilayer under two different voltage conditions as well as the resulting difference spectrum. The cross hatched areas give the total amount of lithium moved by the voltage change.

Impact: Measurement of thickness and composition of surface layers on high technology devices are crucial manufacturing quality control parameters. Company A was able to correlate the results of our measurements with the conditions of the film making process, principally the nitrogen/argon ratio of the CVD plasma, thereby optimizing the process. The lithium profiles for Company B confirmed and quantified the lithium migration in the films, something that was only surmised before our measurements.

Three-Dimensional Compositional Mapping For Industrial Customers

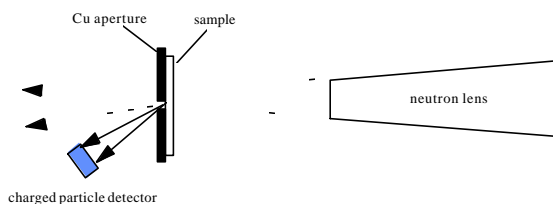


Fig.1. Schematics of experimental setup.

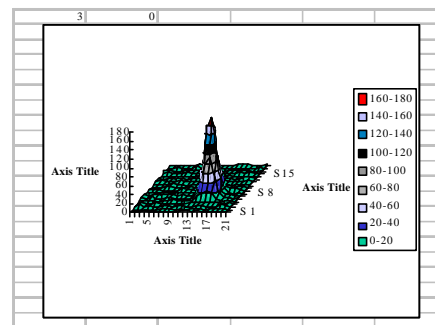


Fig.2. Charged particle response as sample is scanned across the focus.

Project Description: To develop and evaluate new neutron depth profiling (NDP) procedures to increase NIST capabilities for three-dimensional compositional mapping of advanced materials. NDP is a non-destructive technique for determining the near-surface distribution and concentration of certain light elements in materials (such as B in Si). By using a focused neutron beam, we can add lateral spatial resolution to NDP for three-dimensional compositional mapping.

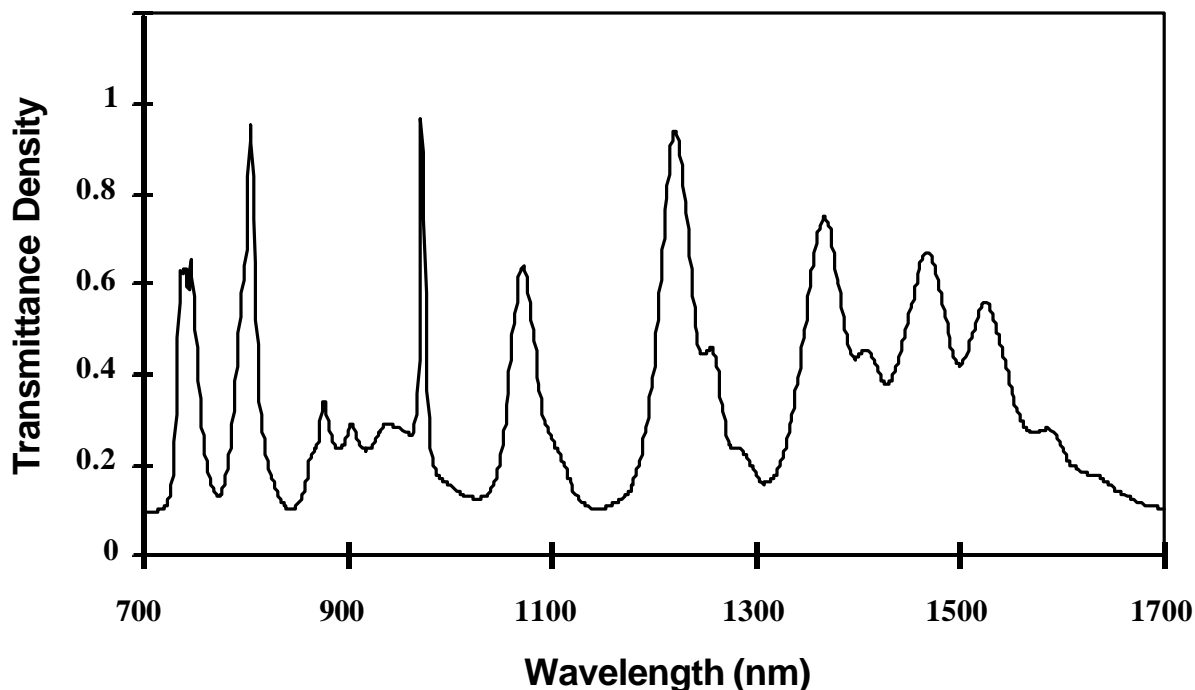
Results: At the sample position, a monolithic lens installed in the NDP chamber increased the neutron current density by a factor of 9 within an area of diameter of 0.12 mm (FWHM of the Gaussian distribution of the focused beam). A preliminary test which involved moving a sample (boron in glass) with compositional variation across the focused beam and measuring the charged particle response demonstrated that the observed spatial resolution for that particular sample was below 0.25 mm.

An automated scanning routine, schematically shown in Fig.1, can be used to search for the maximum charged particle response. The sample (a thin ^{10}B surface deposit) is defined by an aperture of $200\text{ }\mu\text{m} \times 200\text{ }\mu\text{m}$, and scanned over an area of 0.25 mm^2 with a 0.05 mm step size. (See Fig.2.)

Relevance: NDP can provide depth distribution and concentration of critical elements such boron and nitrogen in semiconductor materials. In addition, a higher intensity neutron beam, focused onto a small spot, allows NDP to provide 3-dimensional compositional mapping information. This enhanced capability will facilitate the study of lateral distribution of elements and enable assessment of film uniformity by rastering the sample. It will benefit many NDP applications in the materials research and semiconductor industry, including assessing the distribution of various elements such as boron, lithium, and/or nitrogen in semiconductor materials and in new materials such as synthetic diamonds.

Process Monitoring

Near Infrared Transmission Wavelength Standards

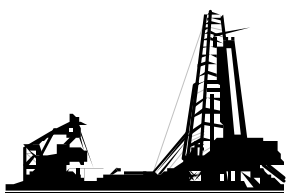


Project Description: Identify and qualify potential optical wavelength standards for the near-infrared (NIR) spectral region for industrial manufacturers and users of NIR spectrophotometers.

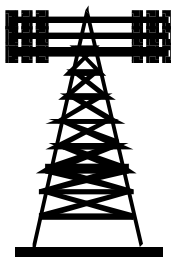
Results: Feedback from an exercise in which prototype rare earth oxides-in-glass filters were sent to a variety of users resulted in a new formulation that includes holmium oxide. This new formulation introduces additional absorbance peaks in the 1000 nm to 2500 nm region and will be suitable for use with dispersive as well as with Fourier transform instruments.

Relevance: NIR spectroscopy can be used for nondestructive, qualitative, and quantitative chemical analysis with little, if any, sample preparation and increasingly is being used in the pharmaceutical, chemical and agricultural industries; however, lack of a relevant standard is significantly impeding the implementation of NIR methods.

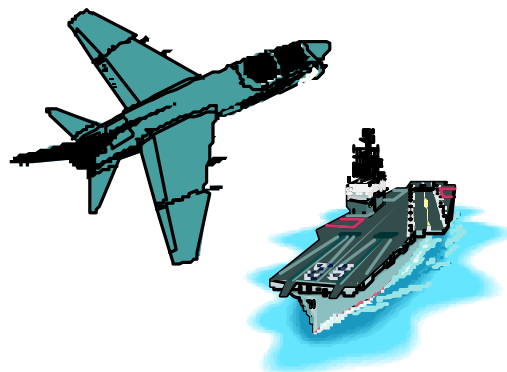
Evaluation of the Accuracy of Karl Fischer Methods Used for the Determination of Water in Oils



CRUDE OIL



TRANSFORMER OIL



HYDRAULIC OILS

Project Description: Sources of variation and bias among various Karl Fischer titration systems used for the measurement of moisture in oils are being systematically investigated and needed reference materials are being developed.

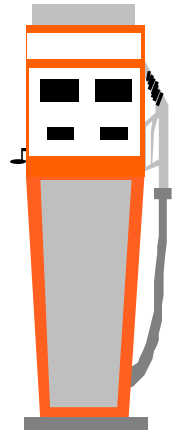
Results: Several sources of systematic bias have been identified including: factory calibration of instruments; incorrect settings of operator adjustable parameters; titration cell geometry; and solubility of the oil in the titration solvent. In addition to SRMs already provided by NIST with certified values for water in mineral oil, transformer oil, and methanol, a new SRM, *Water Saturated Octanol* is under development to aid in calibrating Karl Fischer titrations.

Relevance: The performance and price of oils are a function of their water content. ASTM-sponsored collaborative studies using ASTM-approved methods revealed unacceptable variability (~20% to 50%) in moisture in oil determinations. The oil industry, electric power industry, and the military need accurate methods and reference materials to assess the water content of their oils.

Automotive New Gasoline Based Standards

SRMs 2286-2297

- Reformulated gasolines developed to address compliance with the Clean Air Act of 1990
- All gasoline has to be tested at the refinery and at the point of delivery
- Two billion liters of gasoline produced in the U.S./day
- 8 SRMs certified for oxygenate content
- 4 SRMs certified for sulfur, benzene, total aromatics, total oxygen, and total olefin content



New Technologies Developed

“Liposome Immunoanalysis by Flow Injection Assay”

-Licensed by Saddleback Aerospace

“An Efficient Drift Correction Procedure”

-Invention Disclosure Filed